Oximidocarbonic Esters and Related Compounds

A Thesis

by

Ralph Edward Oesper

Submitted to the Faculty of the Graduate School of the University of Cincinnati, in fulfillment of part of the requirements for the Degree of Doctor of Philosophy.

Cincinnati, Ohio,

June, 1914.

The oximidocarbonic esters, i.e., compounds of the formula $RO-\underset{\underset{NOH}{|}}{C}-OR$, may be of two types, simple esters in which the two radicals are alike, and mixed esters in which they are different. The latter type is especially interesting, since it offers the possibility of obtaining geometric stereoisomers in syn-and anti-modifications. This work was undertaken in the hope of isolating these stereoisomers, and, also, with the intention of investigating their behavior when they are subjected to the action of reagents which bring about the Beckmann rearrangement of oximes, etc.

We found that the preparation of the simple oximido esters offered no special difficulties, since they could be obtained from imidocarbonic esters by the action of hydroxylammonium chloride.

$$RO-\underset{\underset{NH}{|}}{C}-OR + NH_3[OH]Cl = RO-\underset{\underset{NOH}{|}}{C}-OR + NH_4Cl$$

By this method Houben and Schmidt [1] have recently

[1]. Houben and Schmidt, Ber., 46, 2458[1913].

prepared the diethyl and the dimethyl derivatives. The simple imidocarbonic esters are obtained by the action of bromocyanogen on a mixture of alcohol and its sodium alcoholate. This reaction may be represented by the following equations

I. $BrCN + ROH = Br-C(=NH)-OR$

II. $Br(R)(RO)C = NH + NaOR_1 = (R_1O)(RO)C = NH + NaBr$

In this way Nef [1] prepared the diethyl and diphenyl esters, and Hantzsch [2] the di-p-bromophenyl ester. When sodium phenolate was allowed to react with bromocyanogen in the presence of ethyl alcohol, Nef [3] observed that the ethylphenyl ester, as well as the diphenyl derivative, resulted. This is obvious, since any alcohol may take part in the second stage of the process repre-

[1]. Nef, Ann., 287, 313, 319 [1895].
[2]. Hantzsch and Mai, Ber., 28, 2469 [1895].
[3]. Nef, Loc. cit., 321.

resented above. At first glance this would seem to afford a method of preparing the mixed imidocarbonic esters, but a mixture of two, and possibly three, substances might result, and their separation would be practically impossible, since these compounds cannot be distilled without considerable decomposition.

A reaction described by Nef offered a method for the preparation of the mixed imidocarbonic esters. By the action of sodium ethylate on cyanimidocarbonic ethyl ester, he obtained imidocarbonic ethyl ester.

$$C_2H_5O-\underset{\underset{NH}{|}}{C}-CN + NaOC_2H_5 = C_2H_5O-\underset{\underset{NH}{|}}{C}-OC_2H_5 + NaNC$$

By using other alcoholates in place of sodium ethylate, the desired imido compounds may be obtained, which, on treatment with hydroxylammonium chloride, would give the mixed oximidocarbonic esters.

Thus

$$C_2H_5O-\underset{\underset{NH}{\|}}{C}-CN + NaOR = C_2H_5O-\underset{\underset{NH}{\|}}{C}-OR + NaNC$$

[1]. Loc.cit., p.286

$$C_2H_5O-C(=NH)-OR + NH_3[OH]Cl = C_2H_5O-C(=NOH)-OR + NH_4Cl$$

Preliminary experiments indicate that these reactions take place readily when aliphatic alcoholates [including sodium benzylate] are allowed to react with the cyanimidocarbonic ester, but sodium phenolate and α and β naphtholate react very slowly, if at all, and then give rise to thick, black oils from which it was not possible to extract any of the desired imidocarbonic esters. A further study of the influence of the acid character of the aromatic alcohols will be made later.

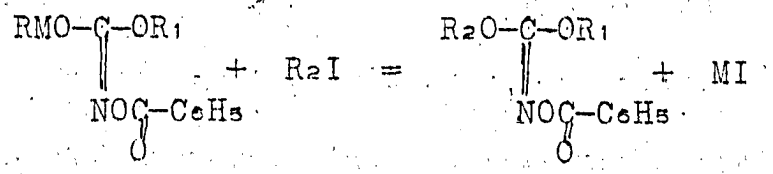
Experiments were also carried out in which attempts were made to extend a method used by Nef [1] for the preparation of cyanimidocarbonic ethyl ester to other compounds of the type $RO-C(=NH)-CN$. By the action of potassium cyanide upon an alcoholic solution of bromcyanogen he obtained cyanimidocarbonic ethyl ester,

[1]. Nef, Loc.cit., p.293.

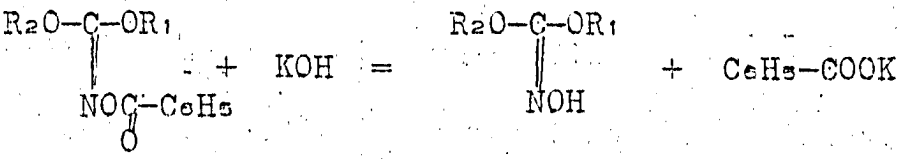
but when isoamyl alcohol or phenol was substituted for the ethyl alcohol in the hope of obtaining the corresponding isoamyl or phenyl ester, the chief product of the reaction was a black tar and the alcohol or the phenol apparently had taken no part in the reaction. When an aqueous solution of the cyanide was slowly added to an ether solution of the bromcyanogen and the alcohol at temperatures not exceeding −5° a greenish yellow oil was formed which changed to a black semi-solid mass as soon as the temperature rose to 10°. Although these experiments were repeated under the most varied conditions, using dilute or concentrated solutions of the cyanide, or even adding powdered cyanide to a moist ether solution of the other materials, a definite product was not obtained and further efforts to prepare these compounds in this way were abandoned.

It seemed probable that the mixed oximido esters might be prepared by the following method; The salts of the acyl derivatives of carbalkyloxyhydroxamic acids

when treated with alkyl halides, might be expected to give acylated oximidocarbonic esters



On careful hydrolysis with alkalies, the acyl radical might be eliminated



If the silver salts correspond to Formula I, then the reaction outlined above would lead to the desired compounds, but if they react according to type [II] isomeric derivatives, $\begin{matrix} O{=}C{-}OR_1 \\ R_2{-}NOH \end{matrix}$ would be obtained. When such possibilities exist, the silver salt usually gives compounds in which the alkyl group is bound chiefly to oxygen, while the sodium salt leads to the corresponding nitrogen derivative. In the cases investigated so far, viz., those in which the ethyl group or the isoamyl group was introduced, we have found that the silver salts gave rise to nitrogen esters, the resulting com-

pounds,when hydrolyzed with hydrochloric acid,yielded β-substituted hydroxylamines,which proved that the alkyl group was bound to notrogen. Under the same treatment,the isomeric oxygen derivatives would have yielded hydroxylamine itself. Furthermore,compounds of the form $\begin{matrix} RO-C-OR \\ \| \\ NO-C-R \\ O \end{matrix}$ have been prepared,and were found to be crystalline solids,while the nitrogen alkyl derivatives obtained by us were oils,which did not solidify even when cooled to -20°. It is possible that moist silver oxide may form silver salts with the metal bound to oxygen,just as Tafel and Enoch [1] have assumed to be the case for amides,or that some of the other compounds of the type $\begin{matrix} HO-C-OR \\ \| \\ NO-C-R \\ O \end{matrix}$,may give the desired mixed oximido esters.

We have found that some of these silver salts may be obtained in two forms,white and yellow,which

[1]. Tafel and Enoch,Ber.,23,104[1890],Meyer and Jacobson,Lehrbuch,Vol.I,p.615.

under proper conditions may be converted into one another. It is possible that these may be the oxygen and nitrogen silver salts, i.e., correspond to Formula I and II respectively. In this case by choosing the proper conditions it should be possible to form the desired compounds. These silver salts will be described at length somewhat later. Then again it may be that the oxygen esters actually were formed first, and that the conditions of our experiments have not been chosen properly to prevent their rearrangement to N-esters, in much the same way that imido esters have been found to rearrange to give alkyl amides.[1]

When the sodium salt of the benzoyl ester of carbethoxyhydroxamic acid was allowed to react with the ethyl iodide in the presence of alcohol, a liquid was obtained which boiled constantly within one degree. But the figures of the analysis did not agree with the values calculated for the ethyl derivative, and, on investigation,

[1]. Comstock and Wheeler, Am. Chem. J. 13, 522[1891], Wheeler, 21, 1865[1899], 23, 140.

the liquid was found to be a mixture of o-ethyl carb-, ethoxyhydroxamic acid and benzoic ethyl ester. During the process, alcoholysis had taken place to give the sodium salt of carbethoxyhydroxamic acid and benzoic ethyl ester and the reaction had proceeded as follows,[1]

[I] $O{=}C(-OC_2H_5)(HN-OC(=O)-C_6H_5) + C_2H_5ONa = O{=}C(-OC_2H_5)(HN-ONa) + C_6H_5C(=O)-OC_2H_5$

[II] $O{=}C(-OC_2H_5)(HN-ONa) + C_2H_5I = O{=}C(-OC_2H_5)(HN-OC_2H_5) + NaI$

The action of the alcohol-free salt will be studied later. However, since the silver salts gave nitrogen alkyl derivatives, the sodium salts will probably do the same, so that this method, in its present form at least, does not seem to be practicable for the preparation of the oximidocarbonic esters.

Carbethoxyhydroxamic acid[hydroxyurethane], $O{=}C(-OC_2H_5)(H-N-OH)$

[1]. Compare Titherly, J. Am. Chem. Soc., 79, 392[1901].

was first prepared by Hantzsch [1]. Jones [2] modified the method of preparation and also studied some of its alkyl and acyl derivatives. This modified method has now been applied to the preparation of several of the homologues of carbethoxyhydroxamic acid. The benzoyl esters of these compounds are readily obtained by treating the aqueous solution of with benzoyl chloride in the presence of potassium carbonate. The silver salts of these esters are obtained if aqueous silver nitrate is added to an alcoholic solution of the ester, to which the equivalent quantity of ammonium hydroxide has been added.

When treated in this way, all of the compounds investigated produce bright yellow silver salts, but while the yellow color of the methyl, ethyl and prophyl compounds is permanent, the yellow precipitates produced in the case of the higher members of the series immediately become colorless. The precipitates are pro-

[1]. Hantzsch
[2]. Jones

duced in curds and if one of these lumps is broken the interior is found to be of the original yellow color. Whether the change is due to contact with the alcohol or the water, or whether the phenomenon is a photochemical one has not yet been definitely determined. The white salts are more sensitive to the light than the yellow ones and blacken readily even if preserved in an amber desiccator.

Interestingly enough, these salts, both the yellow and the white, are slightly soluble in ether and readily dissolve in chloroform and benzene. When alcohol is added to these solutions, bright yellow needles are precipitated regardless of the original color of the salt. The yellow salts thus produced are perfectly stable, scarcely affected by light and show no tendency to change to the white forms at room temperature. At higher temperatures, however, the conversion is rapid, and the resulting white modifications are also stable at room temperature, even in contact with the yellow

variety. No decomposition occurs during this change, neither is there any apparent change in the crystalline form, and both modifications have the same ultimate composition, which is that of the simple salts, without any solvent of crystallization. Therefore the two forms must represent either polymers or tautomers.

The yellow silver salt of the benzoyl ester of carbisoamyloxyhydroxamic acid changes to the white modification rapidly at about 75°, and it seemed possible that the molecular weight in boiling benzene [B.P. 80.5°] might differ from the value as determined by the freezing point method. If the same value was obtained it argued for a tautomeric change, while if the values were multiples of each other polymerization would be indicated. The values actually obtained, however, were not conclusive. Association of two or more molecules was indicated, and furthermore, the molecular weight of these complexes increased with the concentration of the solutions. No change in color was apparent when

the solution was raised to the boiling point and the change which occurs when the dry salt is heated probably does not take place in solution. All of the white salts investigated so far dissolve in chloroform or benzene to form yellow solutions from which alcohol precipitates the yellow salt. As mentioned above, when prepared in alcoholic solution the yellow salts become white on the surface where they are in contact with the solvent. Furthermore, if the yellow salts are precipitated from chloroform or benzene solutions are dried and then suspended in alcohol, they gradually lose their color and go over to the white form. Therefore it appears that low temperature and the presence of chloroform, benzene [and ether] favor the yellow form, while alcohol, water and higher temperature stabilize the white salts. No solvent has been found in which the white salts do not change to the yellow form, so it does not seem possible to determine their molecular weight at present. All the chemical evidence in-

dicates that the yellow salts have the silver bound to nitrogen,but as these reactions were carried out in the presence of ether which favors the yellow form it may be that if alcohol [which favors the white form] is used as the medium,alkyl halides may react to give compounds in which the alkyl group will be bound to oxygen. Such results,of course,would prove without doubt that the white and yellow salts are tautomeric. These experiments will be carried out. Likewise,attempts will be made to prepare the carbalkylhydroxamic acids containing large aromatic radicals in oreder to study the effect of such groups on the relative stability of the white and yellow forms.

Experimental Part.

Derivatives of Carbalkyloxyhydroxamic Acids, $\begin{matrix} O=C-OR \\ H-N-OH \end{matrix}$

The only one of these compounds which has been described is the ethyl derivative prepared by Hantzsch and later by Jones. It seemed desirable to prepare some of the homologues of this compound as they are the materials from which it seemed possible, as was outlined above, to obtain the oximidocarbonic esters. The method used by Jones [1] for preparing carbethoxyhydroxamic acid was used to prepare the corresponding methyl, propyl, isoamyl and benzyl derivatives. The procedure is as follows. One equivalent quantity of hydroxylammonium chloride is pulverized and thoroughly mixed with two equivalents of powdered potassium carbonate. The mixture is covered with moist ether and one equivalent of the chlorcarbonic ester is added in small portions, the flask being cooled with running water. After all the chloro-

[1]. Jones, Amer. Chem. J. 20, 41.

carbonate is added the flask is connected with a reflux condenser and the reaction mixture allowed to stand until the evolution of carbon dioxide has ceased[10 or12 hours].

$$\begin{matrix} O{=}C{-}OR \\ | \\ Cl \end{matrix} + NH_3[OH]Cl + K_2CO_2 = \begin{matrix} O{=}C{-}OR \\ | \\ H{-}N{-}OH \end{matrix} + 2KCl + CO_2 + H_2O$$

After removing the potassium chloride by filtration, the ether is washed with a small quantity of water,and dried over fused sodium sulphate. The ether is then distilled and the remaining oil is placed in a desiccator which is exhausted for several hours to remove the last traces of ether. In this way colorless or slightly yellow oils possessing a characteristic odor were obtained. The benzyl derivative is a crystalline solid. When treated with ferric chloride solution these compounds give a deep blue or purple color reaction and they immediately reduce ammoniacal silver nitrate.

As mentioned above,the benzoyl esters of these compounds, $\begin{matrix} O{=}C{-}OR \\ | \\ H{-}N{-}OC{-}C_6H_5 \\ \| \\ O \end{matrix}$, are formed when their aqueous

solutions are treated with benzoyl chloride in the presence of potassium carbonate. These esters can be purified by extracting their ether solutions with sodium hydroxice. If carbon dioxide is passed through the alkaline solution, the esters are precipitated. However, these compounds are very easily hydrolysed by dilute alkalies, even in the cold, and a large part of the product is usually lost in this way.

Derivatives of Carbmethoxyhydroxamic Acid.

Carbmethoxyhydroxamic Acid, $O{=}C(-OCH_3)(-N(H)-OH)$ ——Twenty-five grams of chlorcarbonic methyl ester, 18.4 grams of hydroxylammonium chloride and 36.5 grams of potassium carbonate produced 21 grams of a thick yellow oil which was very soluble in water. This was not analyzed but was converted into its benzoyl ester.

The Benzoyl Ester of Carbmetoxyhydroxamic Acid, $O{=}C(-OCH_3)(-N(H)-O-C(=O)-C_6H_5)$——

To 9 grams of carbmethoxyhydroxamic acid and 6.8 grams of potassium carbonate dissolved in water, 13.8 grams of benzoyl chloride was added in small portions. A colorless

oil separated which soon solidified. When recrystallized from warm chloroform and ligroin it formed white needles melting at 82°. The yield was 12.5 grams.

0.2550 g. gave 17 cc. N_2 at 29° and N746 mm.

Calc. for $C_9H_9O_4N$ N,7.18. Found N,7.16%.

The compound was soluble in ether, alcohol and chloroform, insoluble in water and in cold ligroin.

The Silver Salt of the Benzoyl Ester of Carmetoxyhydroxamic Acid, $Ag-N(-O-C(=O)-OCH_3)-C(=O)-C_6H_5$——Nine grams of the benzoyl ester described above was dissolved in alcohol and the equivalent quantity of ammonium hydroxide was added to it. This solution was treated with 7.8 grams of silver nitrate dissolved in water and a bright yellow precipitate was formed which was filtered, washed with alcohol, and water, and dried on a clay plate. Yield, 11 grams.

0.4870 g. gave 0.1735 g. Ag.

Calc. for $C_9H_8O_4NAg$ Ag,34.74. Found Ag,35.62%.

The salt melts at 149–150°, is very stable toward light and is the only one of the silver salts investigated.

which was not soluble in chloroform or benzene.

Derivatives of Carbethoxyhydroxamic Acid.

The Silver Salt of the Benzoyl Ester of Carbethoxyhydroxamic Acid, $O{=}C(-OC_2H_5)-N(-Ag)-OC(=O)-C_6H_5$ — Forty grams of this salt [1] were obtained by the action of 30 grams of silver nitrate on 37 grams of the benzoyl ester of carbethoxyhydroxamic acid. After the salt was dried it was dissolved in warm chloroform, the solution filtered and cooled to −5°. Alcohol was then added and a mass of bright yellow needles was precipitated. These were filtered off and dried on a porous plate.

0.3540 g. gave 0.1210 g. Ag.

Calc. for $C_{10}H_{10}O_4NAg$ Ag, 34.15. Found Ag, 34.18%.

The salt is readily soluble in chloroform and benzene, slightly soluble in ether and insoluble in alcohol. When heated to 156–157° the yellow color fades and a pure white mass results which darkens rapidly if the temperature is raised beyond this point. The salt melts with

[1]. Jones, Loc.cit., p.49.

decomposition at 174°. The white form is stable at room temperature though it is much more sensitive to light than is the yellow variety. A sample on ignition gave the following figures

0.4356 g. gave 0.1489 g. Ag.

Calc. for $C_{10}H_{10}O_4NAg$ Ag,34.15. Found Ag,34.18%.

N-Ethyl Derivative of the Benzoyl Ester of Carbethoxyhydroxamic Acid, $C_2H_5N(-OC(=O)-C_6H_5)-C(=O)-OC_2H_5$ ——Twenty-seven grams of ethyl iodide were added to 50 grams of the silver salt suspended in ether, and the mixture was allowed to stand in the dark for two weeks. At the end of this time the bright yellow color of the silver salt had disappeared. The silver iodide was separated by filtration and washed with ether. After shaking the ether solution with a solution of sodium thiosulphate to remove the small quantity of iodine that had separated, it was dried with fused sodium sulphate and freed from ether by distillation. The light yellow oil which remained was fractionated in vacuo. After three fractionations, 10

g. were obtained which boiled with slight decomposition at 188–190° under a pressure of 25 mm.

0.1526 g. gave 8.64 cc. N_2 at 29° and 743 mm.

Calc. for $C_{12}H_{15}O_4N$ N,5.90. Found N,6.09.

The substance was an oil with a spicy odor. It was nearly insoluble in water, but soluble in most organic solvents.

Hydrolysis of the Ethyl Derivative by Hydrochloric Acid.—Three and seven-tenths grams of the oil were heated with 10 cc. of concentrated hydrochloric acid in a sealed tube for six hours at 105°. When the tube was opened, carbon dioxide and ethyl chloride escaped. The contents of the tube were extracted with ether, and 1.4 g. [calculated 1.5 g.] of benzoic acid were obtained when the ether was evaporated. The water solution was concentrated over a water bath until a thick yellow oil remained which would not solidify even at −10°. It was identified as β-ethyl hydroxylammonium chloride by condensing it with para-nitrobenzaldehyde. The con-

densation product melted at 123°, which agrees with the value given by Hantzsch [1] for N-ethyl-p-nitroisobenzaldoxime, $[NO_2]C_6H_4-\underset{\underset{O}{\diagup}}{\overset{H}{\overset{|}{C}}}-NC_2H_5$. Therefore, the ethyl group was bound to nitrogen, since hydroxylamine would have been produced by the hydrolysis of the ethoxy derivative. The hydrolysis may be represented as follows

$$C_2H_5-NO\overset{O=C-OC_2H_5}{\overset{|}{C}}(=O)-C_6H_5 + H_2O + 2HCl = CO_2H + C_2H_5Cl + C_6H_5COOH + C_2H_5-NH_2[OH]Cl$$

A sample which had not been distilled gave the same products when hydrolysed showing that no rearrangement of the o ethyl derivative had taken place during the distillation.

N-Isoamyl Derivative of the Benzoyl Ester of Carbethoxyhydroxamic Acid, $C_3H_{11}-N(-O-\overset{O=C-OC_2H_5}{\overset{|}{C}}(=O)-C_6H_5)$ — Eleven and nine-tenths grams of isoamyl iodide were added to 19 g. of the silver salt of the benzoyl ester of carbethoxyhydroxamic acid suspended in ether. After two weeks the silver iodide was removed and the product was treated

[1]. Hantzsch and Hillard, Ber., 31, 2066 [1898].

in the manner described under the ethyl derivative. After three fractionations, 16 g. of a yellow oil, boiling, with slight decomposition, between 203–205°, at 30 mm. were obtained.

0.1562 g. gave 7.9 cc. N_2 at 31° and 745 mm.

Calculated for $C_{18}H_{21}O_4N$ N, 5.01. Found N, 5.10.

The substance resembled the ethyl derivative described above in all of its properties.

The Hydrolysis of the N-Isoamyl Derivative with Hydrochloric Acid.——Three grams of the oil were heated with 10 cc. of concentrated hydrochloric acid in a sealed tube for three hours at 100°. Carbon dioxide and ethyl chloride escaped on opening the tube. One and two-tenths grams of benzoic acid [calculated 1.3 g.] were extracted with ether and the water gave brownish crystals when evsporated. These crystals were dissolved in water and a turbid suspension was produced by the addition of ether. An alcoholic solution of platinic chloride precipitated a yellow solid substance, which was analyzed –

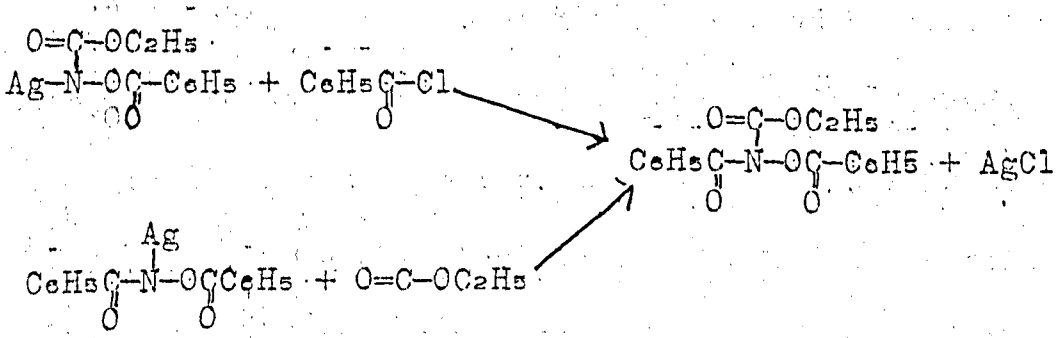
0.0960 g. gave 0.0310 g. of Pt.

Calc. for $[C_5H_{11}NH_2OH]_2PtCl_6$ Pt,31.63. Found Pt,32.29.

In this case,also,the alkyl group was bound to nitrogen.

Structure of the Silver Salt.

The formation of these products indicate that the silver salt has the silver bound to nitrogen. If this is true it is evident that the compound produced by the action of chlorcarbonic ester on the silver salt of dibenzhydroxamic acid should be identical with the substance formed by the action of benzoyl chloride on the silver salt under discussion. These reactions are shown by the following equations:



[a] Action of Benzoyl Chloride on the Silver Salt

of Carbethoxyhydroxamic Acid.—Eleven and five-tenths grams of the silver salt suspended in ether, were treated with 5 grams of benzoyl chloreide. After standing four hours, the silver iodide was filtered off, and the ether was removed by distillation. Eight grams of a colorless oil remained which slowly deposited transparent prismatic crystals. When recrystallized from ether and ligroin, the compound melted at 71–72°.

[b] Action of Chlorcarbonic Ethyl Ester on the Silver Salt of Dibenzhydroxamic Acid——Five grams of the silver salt of dibenzhydroxamic acid [1] were treated with 1.5 grams of chlorcarbonic ethyl ester in the presence of ether. After two weeks, the silver chloride and the unchanged silver salt were removed by filtration, and the ester evaporated in vacuo. After standing for several days, the odor of the ester had disappeared and the remaining oil slowly solidified. The crystals melted at 71–72°, and a mixture of the products of the reactions described under [a] and [b] melted at the same

temperature.

The same product resulted from bothe of these reactions and it was identical with the dibenzoyl ester of carbethoxyhydroxamic acid described by Jones [1] who prepared it from the sodium salt of the benzoyl ester of carbethoxyhydroxamic acid and benzoyl chloride.

The Action of Ethyl Iodide on the Sodium Salt of Carbethoxyhydroxamic Acid—To a solution of 35 g. of benzoyl ester of carbethoxyhydroxamic acid in alcohol, 3.8 g. of sodium, dissolved in alcohol, and 26g. of ethyl iodide were added. After two weeks the alcohol was removed by distillation and the mixture of crystals and oil which remained was extracted with ether. After washing the ether with water, it was dried with sodium sulphate and distilled. A colorless oil was obtained which was fractionated in vacuo, 24 g. of a clear colorless liquid, boiling at 108-109° at 25 mm. resulting.

The figures which the analysis of the oil gave did not agree with the values calculated for the ethyl

[1] Jones,

derivative, and, on further investigation, it was found that the oil consisted of a neutral and an acid portion. It was dissolved in ether and shaken with a solution of sodium hydroxide. The neutral portion was found to be ethyl benzoate, boiling at 213°. The alkaline solution was acidified and extracted with ether. A clear, colorless liquid was obtained which boiled between 96–97° at 17 mm. When treated with phosphorus pentachloride and then with water and alkalies, it gave a base whose chloride melted at 127°. This chloride formed a chloroplatinate which melted with decomposition between 174–176°.

0.096 g. gave 0.0352 g. Pt.

Calc. for $[C_2H_5OHN_3]_2PtCl_6$ Pt, 36.65. Found Pt, 36.66.

These results showed that the compounds under consideration were derivatives of α-ethylhydroxylamine.

The acid portion was therefore o-ethylhydroxyurethane. It was found to be identical with the ethyl derivative described by Jones. [1] The origin of these products

[] Jones,

was explained above.

Derivatives of Carbpropyloxyhydroxamic Acid.

Carbpropyloxyhydroxamic Acid, $\begin{matrix} O=C-OC_3H_7 \\ | \\ H-N-OH \end{matrix}$ ——Twenty-five grams of chlorcarbonic propyl ester were added to a mixture of 14.2 grams of hydroxylammonium chloride and 28 grams of potassium carbonate. 22.5 grams of a thick colorless oil were obtained which were converted into the benzoyl ester.

Benzoyl Ester of Carbpropyloxyhydroxamic Acid, $\begin{matrix} O=C-OC_3H_7 \\ | \\ H-N-O\underset{\underset{O}{\|}}{C}-C_6H_5 \end{matrix}$, Twenty-seven grams of a colorless oil were obtained by the action of 20 grams of carbpropyloxyhydroxamic acid, 11.5 grams of potassium carbonate and 23.5 grams of benzoyl chloride. All attempts to solidify the oil were unsuccessful. Accordingly, it was dissolved ~~with~~ in alcohol, neutralized with ammonium hydroxide and 21 grams of silver nitrate were added to the solution. A bright yellow precipitate was obtained. This was crystallized from chloroform and alcohol and formed yellow needles melting at 144–145°.

0.4360g. gave 0.1418 g. Ag.

Calc. for $C_{11}H_{12}O_4NAg$ Ag,32.67. Found Ag,32.52%.

When heated,this salt gave no indication of changing to a white modification.

Dibenzoyl Ester of Carbisopropyloxyhydroxamic Acid, $C_6H_5C(=O)-N(-OC(=O)-C_6H_5)-C(=O)-OC_3H_7$——Ten grams of the silver salt described above were suspended in ether and 4.2 grams of benzoyl chloride were added. The reaction was completed in three days. The silver chloride was removed by filtration and the ether evaporated in vacuo. 9 grams of a thick oil remained which slowly deposited transparent cubical crystals. These were recrystallized from chloroform and ligroin and melted at 78–79°.

0.2822 g. gave 11.4 cc. N_2 at 28° and 745 mm.

Calc. for $C_{18}H_{17}O_5N$ N,4.28. Found N,4.36%.

This compound is soluble in ether,chloroform and alcohol and insoluble in cold ligroin and water.

The N-Ethyl Derivative of the Benzoyl Ester of Carb-

propyloxyhydroxamic Acid, $C_2H_5-\underset{\displaystyle O}{\overset{\displaystyle O=C-OC_3H_7}{\overset{|}{N}}}-OCC_5H_5$ —Fifteen grams, of the silver salt described above were suspended in ether and 7 grams of ethyl iodide added. After standing two weeks in the dark, the silver iodide was filtered off and the ether evaporated in vacuo. 9 grams of a light yellow oil with a spicy odor remained.

0.2402 g. gave 12.2 cc. N_2 at 22.5° and 735 mm.

Calc. for $C_{13}H_{17}O_4N$ N, 5.53. Found N, 5.57%.

When heated in a sealed tube with hydrochloric acid β-ethyl hydroxylammonium chloride was obtained. This was identified by condensing it with p-nitrobenzaldehyde. This shows that the alkyl group was bound to nitrogen.

Derivatives of Carbisobutyloxyhydroxamic Acid.

Carbisobutyloxyhydroxamic Acid, $H-\underset{\displaystyle OH}{\overset{\displaystyle O=C-OC_4H_9}{\overset{|}{N}}}$ —Twenty-five grams of chlorcarbonicisobutyl ester, 12.8 grams of hydroxylammonium chloride and 25 grams of potassium carbonate produced 21 grams of a colorless oil which was not very soluble in water. When treated with copper acetate solution it produced a crystalline green precipi-

tate which was not affected when boiled with water.

Benzoyl Ester of Carbisobutylhydroxamic Acid, $H-N(-OC(=O)-C_6H_5)-C(=O)-OC_4H_9$ — A colorless oil was produced by the action of 19 grams of benzoyl chloride, 9.4 grams of potssium carbonate and 18 grams of carbisobutyloxyhydroxamic acid. This was dissolved in ether and extracted with dilute sodium hydroxide. The alkaline solution was cooled to 5° and carbon dioxide passed in. A crystalline precipitate appeared. When recrystallized from warm chloroform and ligroin it formed needles melting at 43–44°. Yield, 19 grams.

0.2944 g. gave 16.5 cc. N_2 at 28° and 751 mm.

Calc. for $C_{12}H_{15}O_4N$ N, 5.90. Found N, 6.09%.

The compound is soluble in ether, chloroform and alcohol, and insoluble in water and cold ligroin.

The Silver Salt of the Benzoyl Ester of Carbisobutyloxyhydroxamic Acid, $Ag-N(-OC(=O)-C_6H_5)-C(=O)-OC_4H_9$ — An alcoholic solution of 21.5 grams of the benzoyl derivative was treated with an equivalent quantity of ammonium hydroxide and then with an aqueous solution of 15 grams of silver ni-

trate. A bright yellow precipitate was formed which immediately became colorless where it was in contact with the solvent. The interior of the precipitate was still yellow after standing five minutes. The precipitate was filtered, and thoroughly washed with alcohol and dried on a clay plate placed in an amber desiccator. After standing over night the entire mass had blackened. This material was extracted with warm chloroform, the solution cooled to −5° and an excess of alcohol added.

0.2492 g. gave 0.0784 g. Ag.

Calc. for $C_{12}H_{14}O_4NAg$ Ag, 31.37. Found Ag, 31.46%.

When warmed to 80–82° the yellow crystals become white. The white mass softens at 144° and finally melts at 158°. The white form is stable at room temperature. A sample on ignition, gave the following results,

0.4230 g. gave 0.1325 g. Ag.

Calc. for $C_{12}H_{14}O_4NAg$ Ag, 31.37. Found Ag, 31.32%.

The conversion of the yellow form into the white takes place very slowly at 40°, but the change occurs only in

certain parts of the mass and the rest of the material remains yellow. Furthermore, the change appears to commence in the interior of these regions and spreads outward indicating that the phenomenon is not of a photochemical nature. The most curious effect, however, is observed if a portion of the white form is rubbed against a hard surface with a porcelain spatula. Where it is rubbed a bright yellow streak appears which immediately becomes colorless again. The rapidity of the reversion to the white form seems to be influenced by the intensity of the light, for the change is almost instantaneous in direct sunlight, slower in diffused light, while if the salt is rubbed in the dark it remains yellow until brought into the light. No explamation of this peculiar behavior is offered.

The Dibenzoyl Ester of Carbisobutyloxyhydroxamic Acid, $C_6H_5C(=O)-N(-OC(=O)C_6H_5)-C(=O)-OC_4H_9$. [To be described later].

The N-Ethyl Derivative of the Benzoyl Ester of Carbisobutyloxyhydroxamic Acid, $C_2H_5-N(-OC(=O)-C_6H_5)-C(=O)-OC_4H_9$ ---Twenty-one -

and five-tenths grams of the yellow silver salt described above were suspended in ether and 10 grams of ethyl iodide added. The reaction was complete after two weeks. A bright yellow oil with a spicy odor was obtained when the ether was evaporated. Yield, 14 grams.

0.3096 g. gave 15.6 cc. at 29° and 740mm.

Calc. for $C_{14}H_{19}O_4N$ N, 5.28. Found N, 5.37%.

When heated in a sealed tube with concentrated hydrochloric acid for six hours at 110°, β-ethyl hydroxylammonium chloride was obtained, showing that this was the nitrogen derivative.

Derivatives of Carbisoamyloxyhydroxamic Acid.

Carbisoamyloxyhydroxamic Acid, $\begin{matrix} O{=}C{-}OC_5H_{11} \\ H{-}N{-}OH \end{matrix}$ —+ Twenty-five grams of chlorocarbonicisoamyl ester, 11.5 grams of hydroxylammonium chloride and 22.8 grams of potassium carbonate were allowed to react in the usual manner, and 23 grams of a thick, light yellow oil were obtained. The compound had a slight odor suggestive of isoamyl alcohol and was only slightly soluble in water. Copper acetate

produces a green crystalline precipitate from an alcoholic solution which was not affected when boiled with water.

The Benzoyl Ester of Carbisoamyloxyhydroxamic Acid, $O{=}C(-OC_5H_{11})-NH-O-C(=O)-C_6H_5$ — All attempts to obtain this compound in the solid state were fruitless. The product of the reaction of carbisoamyloxyhydroxamic acid, potassium carbonate and benzoyl chloride was a colorless oil, which, when dissolved in sodium hydroxide and precipitated by carbon dioxide, remained liquid even when thoroughly dried and cooled to -10° for several hours. It is very easily hydrolyzed by dilute alkalies and the yield is extremely poor if purified in this way.

Silver Salt of Carbisoamyloxyhydroxamic Acid, $O{=}C(-OC_5H_{11})-N(Ag)-O-C(=O)-C_6H_5$ — The silver salt is precipitated from an alcoholic solution of the benzoyl ester in bright yellow curds which turn white immediately. After drying over night it was dissolved in warm chloroform and reprecipitated by alcohol in bright yellow needles.

0.4506 g. gave 0.1354 g. Ag.

Calc. for $C_{13}H_{16}O_4NAg$ Ag,30.13. Found Ag,30.06%.

When heated to 40°,the salt turns white in patches,and at about 75° the change is rapid and complete. If the temperature is raised still higher,no further change occurs until the salt melts at 141–142°. The white form, on ignition,gave the following results,

0.3632 g. gave 0.1090 g. Ag.

Calc. for $C_{13}H_{16}O_4NAg$ Ag,30.13. Found 30.01%.

This white form showed no tendency to revert to the yellow modification,even in contact with a particle of the latter at −10°. On one occasion,the yellow form was precipitated as usual from a chloroform solution by alcohol, and as soon as the crystals were separated from the solvent by filtration they began to turn white. However,the change was localized and after two weeks the yellow and the white forms still existed side by side. We have never beem able to duplicate this change at room temperature.

As was stated above,it seemed possible that mol-

ecular weight determinations might throw more light on the nature of this color change. The figures obtained in freezing benzene gave values which varied from 739 to 1514 depending on the concentration of the solution, and the values in boiling benzene, using Menzies' method, were of the same order. The value for the simple salt is ~~538~~ 358.

Dibenzoyl Derivative of carbisoamyloxyhydroxamic Acid, $C_6H_5C(=O)-N(-OC(=O)-C_6H_5)-O-C(=O)-C_5H_{11}$. [To be described later].

The Ethyl Derivative of the Benzoyl Ester of Carbisoamyloxyhydroxamic Acid, $C_2H_5-N(-O-C(=O)-C_6H_5)-O-C(=O)-C_5H_{11}$—Eleven grams of the yellow silver salt and 4.8 grams of ethyl iodide were allowed to react in the presence of ether for two weeks. A light yellow oil remained when the ether evaporated.

0.4323 g. gave 20 cc. N_2 at 25° and 745 mm.

Calc. for $C_{15}H_{21}O_4N$ N, 5.01. Found, N, 5.06%.

Derivatives of Carbbenzyloxyhydroxamic Acid.

Carbbenzyloxyhydroxamic Acid, $H-N(-OH)-C(=O)-OCH_2C_6H_5$ — Forty grams of chlorocarbonicbenzyl ester, 16.2 grams of hydroxylammonium chloride and 32.4 grams of potassium carbonate

produced a thick yellow oil which solidified on standing over night. When recrystallized from chloroform and ligroin the compound was obtained in shining scales melting at 65°. Yield, 30 grams.

0.2530 g. gave 19.4 cc. N_2 at 28° and 747.5 mm.

Calc. for $C_8H_9O_3N$ N, 8.38. Found N, 8.29%.

The compound is insoluble in ether, alcohol and chloroform, somewhat soluble in water and insoluble in cold ligroin.

The Benzoyl Ester of Carbbenzyloxyhydroxamic Acid, $O{=}C(-OCH_2C_6H_5)-N(H)-OC(=O)-C_6H_5$ ——Eighteen and five-tenths grams of carbenzyloxyhydroxamic acid were treated with 7.46 grams of potassium carbonate and 15.6 grams of benzoyl chloride. An oil separated which was soon solidified. When recrystallized from warm alcohol and ligroin it formed white needles melting at 109–110°.

0.2944 g. gave 13.6 cc. N_2 at 23.5° and 748.5 mm.

Calc. for $C_{15}H_{13}O_4N$ N, 5.16, Found N, 5.12%.

The compound is soluble in alcohol, ether and chloroform

and insoluble in water and cold ligroin.

The Silver Salt of the Benzoyl Ester of Carbbenzyl-oxyhydroxamic Acid, $Ag-N(-O-C(=O)-C_6H_5)-C(=O)-OCH_2C_6H_5$ — Sixteen grams of the benzoyl ester, when treated with ammonium hydroxide and 10.3 grams of silver nitrate gave a yellow precipitate which immediately turned white. When recrystallized from chloroform and alcohol it formed bright yellow needles which melted at 150-151°.

0.3583 g. gave 0.1025 g. Ag.

Calculated for $C_{15}H_{21}O_4NAg$ Ag, 28.67. Found Ag, 28.61%.

The salt becomes white when heated, but the transition temperature is so near the melting point that it was not possible to isolate the white form.

The Dibenzoyl Ester of Carbbenzyloxyhydroxamic Acid, $C_6H_5C(=O)-N(-O-C(=O)-C_6H_5)-C(=O)-OCH_2C_6H_5$. [To be described later].

The Ethyl Derivative of the Benzoyl Ester of Carbbenzyl-oxyhydroxamic Acid, $C_2H_5-N(-O-C(=O)-C_6H_5)-C(=O)-OCH_2C_6H_5$ — Eight grams of the silver salt described above were allowed to react with 3.3 grams of ethyl iodide for one week. 5 grams of a

light yellow oil were obtained.

0.4658 g. gave 20 cc. N_2 at 21° and 745 mm.

Calc. for $C_{17}H_{17}O_4N$ N,4.68. Found N,4.81%.

Derivatives of Oximidocarbonic Esters.

The Benzoyl Ester of Oximidocarbonic Ethyl Ester, $C_2H_5O-C(=N-O-C(=O)-C_6H_5)-OC_2H_5$. ——Three and one-tenths grams of sodium bicarbonate were added to 5 g. of oximidocarbonic-ethyl ester [1] dissolved in 10 g. of water. 5.1 g. of benzoyl chloride were added in small portions, the flask being cooled with running water. A colorless oil separated which was soon solidified to a mass of white crystals. These were collected on a filter, dried, and recrystallized from chloroform and ligroin. They formed fine needles which melted at 148°.

0.2716 g. gave 14.9 cc. N_2 at 29° and 745 mm.

Calc. for $C_{12}H_{13}O_4N$ N,5.90. Found N,5.91.

The compound was soluble in benzene, in alcohol and in

[1]. Houben and Schmidt, Loc.cit.

chloroform,not very soluble in ether,and insoluble in ligroin and in water. Several crystals were added to the ethyl derivative obtained from the silver salt described above,but the oil showed no tendency to solidify,which proved that the latter was not the oxygen ester existing as an under-cooled liquid.

Imidocarbonic Ethyl Isoamyl Ester, $C_2H_5O-\underset{\underset{NH}{\|}}{C}-OC_5H_{11}$ — Five and three-tenths grams of sodium were treated with the equivalent quantity [20g] of isoamyl alcohol in the presence of wther [1]. 22.5 grams of cyanimidocarbonic ethyl ester,prepared from bromocyanogen,potassium cyanide,and alcohol [2] were added to the suspended alcoholate. Heat was developed,the solution became yellow,and sodium cyanide was precipitated. The reaction mixture was heated for two hours in a flask connected with a reflux condenser, and enough water was added to dissolve the sodium cyan-

[1]. Brühl,Ber.37,2066[1904].
[2]. Nef,Loc.cit.,p.293.

ide. After the water solution had been extracted with ether several times, the ether was dried with calcium chloride. Thus, 32 g. of a light yellow oil, possessing a strong basic odor, were obtained when the ether was evaporated. Even at a pressure of 25 mm. the compound could not be distilled without considerable decomposition. Therefore, no analysis of the substance was attempted. Its identity was established by converting it into the corresponding oximido derivative.

Oximidocarbonic Ethyl Isoamyl Ester, $C_2H_5O-\underset{\underset{NOH}{\|}}{C}-OC_5H_{11}$ —

Eight and four-tenths grams of hydroxylamine, dissolved in a small amount of water, were added to 20 grams of the imido ester dissolved in 20 cc. of ether. The mixture was shaken thirty minutes, the water layer was drawn off, extracted several times with ether, and the ether dried with sodium sulphate. 20 grams of a reddish yellow oil were obtained when the ether evaporated. When cooled to -15°, white crystals appeared which melted when they were spread out on a cold clay plate.

0.1754 g. gave 12.8 cc. N_2 at 24.5° and 742 mm.

Calc. for $C_8H_{17}O_3N$ N,7.99. Found N,8.01.

When freshly prepared the substance was practically odorless,but,on standing,the odor of isoamyl alcohol became apparent. The oil was insoluble in water, but soluble in alkalies,and in most organic solvents.

I gratefully acknowledge my indebtedness to Dr. Lauder W. Jones,under whose direction this work was done,for his many helpful suggestions and his never failing interest.